COATINGS. ENAMELS

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LEAD-FREE BORON-ALUMINOSILICATE ENAMELS FOR ORNAMENTAL COPPER ARTICLES

A. P. Zubekhin,[1] E. A. Yatsenko,[1] and E. B. Klimenko[1]

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A lead-free low-melting boron-aluminate glass matrix is developed. Some of its properties are studied: the average adhesion index, the TCLE, the crystallization capacity. Tinted enamels are obtained on the basis of this glass matrix and used to decorate ornamental copper articles.

It is known [1 – 3] that manufacturers of jewelry extensively use low-melting silicate enamels, which, as a rule, contain lead oxides (Table 1).

It can be seen in Table 1 that the vast majority of enamels contain PbO as the glass-forming agent, which makes them low-melting and at the same time, as a consequence of the high toxicity of this oxide, environmentally unsafe. In the context of stringent environmental requirements, it is now important to develop lead-free enamel compositions and technologies for equipment and machinery, as well as for ornamental and decorative articles.

The purpose of the present study was to develop lead-free boron-aluminosilicate enamels for ornamental copper articles, which would possess good consumer properties and satisfy the requirements of the market economy.

In order to obtain a lead-free low-melting enamel composition, barium oxide was introduced instead of lead oxide. The following system was selected as the basic glass matrix: $(Na_2O, K_2O) – CaO – BaO – B_2O_3 – Al_2O_3 – SiO_2$, in which lead oxide is replaced by barium oxide.

Fifteen glass matrix compositions were investigated in the experiment (Table 2). Batches were prepared from sand and chemical reactants. The glass matrices were melted at 1150 – 1200°C with subsequent exposure at these temperatures for 30 – 40 min and chilling in water. The obtained glass matrices were analyzed to determine their propensity for vitrification and the average adhesion index, which directly depends on the TCLE of the enamel.

The vitrification propensity of the synthesized glass matrices was visually graded as follows:

1 – inhomogeneous crystallization in entire volume;

2 – partial opacification with symptoms of crystallization;

3 – partial opacification;

4 – completely clear glass.

The analysis of the data given in Table 2 led to the following conclusions. Glass compositions 7 – 15 are unsuitable for the development of an optimum glass enamel coat-

[1] South-Russian State Technical University, Novocherkassk, Russia.

TABLE 1

Enamel	Weight content, %						
	SiO_2	B_2O_3	Na_2O	K_2O	PbO	SnO_2	As_2O_5
For jewelry (data of a company in Radeberg)*	55.0	8.6	4.8	5.6	13.0	–	4.0
Low-melting for copper jewelry	34.0	–	–	5.5	56.0	–	4.5
Low-melting frit for jewelry enamel	30.0	–	–	40.0	15.0	15.0	–
For copper and copper alloy jewelry	25.0	–	–	50.0	12.5	12.5	–
Frit for tinted enamels**	31.4	1.7	0.8	6.5	54.1	–	5.2

* Besides, the enamel contained 4.0% F and 5.0% Cu, Fe, Ni, Co, Mn, Cr.

** Besides, the enamel contained 0.5% Al_2O_3.

TABLE 2

Glass matrix composition*	Weight content, %				Vitrification propensity, grade	Properties of coating based on glass matrix	
	Na_2O	K_2O	B_2O_3	SiO_2		average adhesion index, %	TCLE, $10^{-7}\,K^{-1}$
1	15.8	12.2	8.0	44.0	4	74	135
2	17.5	13.7	4.8	44.0	4	78	143
3	18.1	13.9	8.0	40.0	4	76	140
4	15.8	12.2	8.0	44.0	4	74	135
5	13.1	10.1	11.2	45.6	4	81	145
6	16.9	13.1	10.0	40.0	4	74	140
7	14.7	11.3	10.0	44.0	3	72	135
8	17.2	13.2	13.6	36.0	3	68	138
9	13.6	10.4	11.2	44.8	3	65	133
10	18.1	13.9	4.0	44.0	3	65	133
11	12.2	9.4	10.4	48.0	2	63	130
12	18.1	13.9	16.0	32.0	2	62	138
13	15.8	12.2	16.0	36.0	2	60	138
14	13.6	10.4	16.0	40.0	1	58	135
15	13.6	10.4	12.0	44.0	1	58	133

* All compositions contained 5% CaO, 8% BaO, and 7.0% Al_2O_3.

ing, since they become crystallized. Considering that the highest strength of adhesion of glass enamel to metal is accomplished when their TCLE values, in particular, the TCLE of copper ($162 \times 10^{-7}\,K^{-1}$), are as close as possible, glass matrix compositions 2, 3, 5, and 6 were selected for further investigation. As the chemical compositions of these glass matrices are similar, the enamel for ornamental copper articles was developed on the basis of a particular glass matrix (composition 5), which has the highest TCLE.

Various pigments were used in producing glass enamels based on the selected glass matrix. An optimum quantity of each pigment was introduced in an enamel slip in milling. The samples were fired at 850°C. Table 3 shows the results of the study.

It can be seen that lead-free glass matrix 5 without pigment additives makes it possible to produce a claret-colored coating. In this case, ionic tinting of the enamel takes place via diffusion of copper ions, as the consequence of the formation of CuO and Cu_2O crystals in the coating-metal contact layer. The quantities of pigments introduced to obtain tinted enamels differ. Thus, an introduction of 1 – 5% of sky blue, blue pigment, and Cr_2O_3 into glass produces rich deep colors. A further increase in the amount of these additives weakens the luster, deteriorates the color, and leads to various defects in the coating (caking, burns).

TABLE 3

Glass matrix composition	Pigment, oxide	Weight content (above 100%)	Coating color
1	Without additives	–	Claret
2	Sky blue No. 255	1.2	Violet
		5.0	Blue
3	Blue No. 52	1, 2, 5	Turquoise
4	Green No. 61	10.0	Light green
5	Cr_2O_3	1.0	The same
		3.0	Intense green
6	Lemon No. 72	5.0	Orange
		10.0	Light yellow
7	Brown No. 180	10.0	Brown
8	Black No. 1063	10.0	Intense black

However, 10% green, lemon, brown, and black pigment additives ensure rich, bright tones of the indicated colors. A decrease in the content of these pigments prevents obtaining saturated colors, and an increase in their content does not improve the color purity.

Taking into consideration the regularities of the composition theory, an ornamental set has been designed, which is decorated by the specified tinted enamels. The set consists of three pieces: a vase, a tray, and a plaque. The articles have good aesthetic properties, comply with the compositional and color standards, and satisfy the environmental requirements.

Thus, the above studies demonstrate the possibility of using the new lead-free boron-aluminosilicate glass matrix as the basis for decorative enamels for copper.

REFERENCES

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